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**OXIDATIVE MINERALIZATION AND CHARACTERIZATION OF
POLYVINYL ALCOHOL SOLUTIONS FOR WASTEWATER TREATMENT.****ABSTRACT**

Photochemical and ultrasonic treatment of polyvinyl alcohol (PVA), derived from PVA fabric material, with hydrogen peroxide was evaluated as a primary method for PVA mineralization into simpler organic molecules. PVA-based waste streams have been found to be compatible with nuclear process wastewater treatment facilities only when solubilized PVA is more than 90 percent mineralized with hydrogen peroxide. No undesirable solid particles are formed with other nuclear process liquid waste when they are mixed, pH adjusted, evaporated and blended with this type of oxidized PVA waste streams. The presence of oxidized PVA in a typical nuclear process wastewater has been found to have no detrimental effect on the efficiency of ion exchange resins, inorganic and precipitation agents used for the removal of radionuclides from nuclear waste streams. The disappearance of PVA solution in hydrogen peroxide with ultrasonic/ultraviolet irradiation treatment was characterized by pseudo-first-order reaction kinetics.

Radioactive waste contaminated PVA fabric can be solubilized and mineralized to produce processible liquid waste, hence, no bulky solid waste disposal cost can be incurred and the radionuclides can be effectively recovered. Therefore, PVA fabric materials can be considered as an effective substitute for cellulose fabrics that are currently used in radioactive waste decontamination processes.

Keywords: Polyvinyl acetate, peroxide oxidation, ultraviolet and ultrasonic treatment, nuclear process wastewater, decontamination.

INTRODUCTION

Cellulose-based mop heads, wipes and disposable personal protection clothing are currently used as “clean up” products at nuclear facilities. These conventional cleaning materials are used for picking up radioactive spills and mixed waste as well as in general decontamination operations. Cellulose and other polymer-based materials, which can not be laundered or incinerated due to high radioactive contamination, organic constituents or mixed waste characteristics, are disposed in dry active waste streams as bulky solid waste. The increasing cost of final disposal of these types of solid waste makes it necessary to investigate new ways of decreasing radioactive waste treatment and disposal cost.

PVA is a synthetic polymer produced by alkali or acidic hydrolysis of polyvinyl acetate and its molecular weight (7,000-186,000) and percent hydrolysis governs its physical properties such as solubility in hot water. PVA produced from the hydrolysis of polyvinyl acetate, with 88-98 % hydrolysis, dissolves most rapidly in hot water (US patents 5,181,966; 5,507,837 and 5,181,967) and items made from this grade of PVA, especially those without coloring pigments can dissolve in hot water at approximately 90-100 °C. The resulting organic PVA solution, without chemical modification to simpler organic molecules, is not compatible with nuclear process wastewater storage and processing facilities. The processing problems from such unadulterated PVA-based liquid waste, such as “skin” formation, coating of ion exchange materials and poor pumpability stems from the high organic content of the PVA solution.

In this paper, we describe photochemical and ultrasonic treatment of PVA solutions in the presence of hydrogen peroxide along with PVA-nuclear waste compatibility and potential for PVA solution interactions which may affect ion exchange utilization for radioactive wastewater processing in a nuclear waste environment.

Results from this study could serve as part of the technical basis for accepting PVA laden waste in nuclear process wastewater storage and processing facilities. The data will also be useful in the modification of Orex[®] commercial process (Orex[®] process is currently used in the solubilizing of PVA) to accommodate PVA chemical degradation features or in the design of an entirely different equipment unit to simultaneously handle solubilizing and chemical degradation of PVA. The data will also be useful for pilot plant testing of such new equipment to treat radioactive laden PVA by oxidation, pH adjustments and destruction of excess oxidizing agent like hydrogen peroxide.

EXPERIMENTAL

High molecular weight PVA solutions were oxidized with hydrogen peroxide with and without the aid of ultrasonic and ultraviolet energies. Colorimetric measurement technique, at 670 nm, was used to monitor the extent of PVA oxidation during oxidation.

After the oxidative processes, both oxidized PVA and unadulterated neat PVA solutions were mixed with a typical nuclear process wastewater simulant at various temperatures and characterized for “skin” formation and reverse dissolution of PVA. The viscosity and pH of neat PVA and oxidized PVA solutions were also monitored for comparison.

The effect of oxidized PVA solution on ion exchange processes for the uptake of radionuclides was also evaluated with two ion exchange materials (crystalline silicotitanate (CST) and monosodium titanate (MST)) for cesium, strontium and plutonium removal and one precipitation agent (tetraphenyl borate (TPB)) for cesium removal.

The experimental set up for the oxidation and measurement of rheological properties of oxidized 5% PVA solutions included the following, model 2000 Labsonic 20 kHz ultrasonic generator (B. Braun, Allentown, PA), model DR/300 UV-VIS spectrophotometer (Hach cooperation, Loveland, CO), multiple wavelength mercury UV lamp (UVP, Upland CA), model TCV 300 forced-piston viscometer (Cambridge Applied System Inc., Medford, Ma) and an orbital shaker (New Brunswick scientific, Edison, NJ). The H₂O₂/UV/ ultrasonic oxidation set up consisted of a multi-wavelength mercury UV lamp (254, 302 and 366 nm), suspended at 10 mm above Pyrex[®] glass Petri-dishes or 150-mL Teflon[®] beaker reaction vessels. Chemicals reagents used included 50 % hydrogen peroxide (Hach, Loveland CO), 5% PVA solution prepared directly from white woven PVA fabric (Isolyser company, Norcross GA), boric acid, iodine, potassium iodide, milli-Q water, CST (UOP (Ionsive IE-911 lot # 999096810002), MST (Allied Signal, Des Plaines, IL) and TPB (Savannah River Plant).

In the preparation of PVA solutions, about 200 grams of PVA fabric pieces was dried in a vacuum oven overnight at 75 °C.

The five percent PVA solution was prepared by slowly dissolving 50.000 ± 0.0001 grams of the oven dried PVA fabric in about 700 mL milli-Q (distilled and de-ionized water) water on a hot plate. The temperature of the hot water was maintained between 90-100 °C. After the complete dissolution of the PVA in about 700 mL of hot water the solution was quantitatively transferred into a 1000-mL volumetric flask and the solution volume brought to mark with milli-Q water. This PVA preparation approach requires continuous stirring of the mixture to prevent the formations of small hydrated PVA balls. These small hydrated balls are not soluble in hot water. It is, however, easier to prepare a 4 or 3% PVA solutions to prevent the formation of these PVA ball suspensions.

A 4% boric acid solution (40 g boric acid per Liter of distilled water) and Iodine solution (12.7 g of iodine, and 25 g of potassium iodide, per Liter of distilled water) were the reagents used for the colorimetric determination of percent PVA in solution.

PVA calibration standards, 0.5% PVA by weight stock solution, was quantitatively prepared by dissolving 0.1000 g of the oven dried PVA fabric in 20-mL of hot distilled water at 100 °C. The 0.0050 % PVA intermediate stock solution used for the calibration curve generation was prepared by quantitatively transferring 10 ml of the 0.5% PVA solution into a 1000-mL volumetric flask and bringing it to volume with hot distilled water. Based on aliquot intermediate stock solutions, the calibration standards were prepared by quantitatively transferring aliquot samples to a 100-mL volumetric flasks and adding 20 mL of 4% boric acid solution and 6 mL of iodine solution to each 100-mL flask. The flask volume was brought to the 100-mL mark with distilled water. Table 1

show ten calibration standards, which were obtained by diluting aliquot samples of the intermediate stock solution to the 100-ml mark in a 100 ml volumetric flask.

This method for determining percent PVA in solution, before or after oxidation, was adapted from an Air Product procedure for determination of PVA concentration in dilute aqueous matrices such as those obtained from the extraction of paper (Hanson 1998). This colorimetric technique is based on the formation of stable PVA green colored complexes with iodine in the presence of boric acid. By performing a wavelength scan with one of the calibration standards from 500 to 800 nm, the maximum absorption band (λ max) of the iodine/PVA complex was determined to be around 670 nm. Results of the wavelength scan and absorption profile are plotted in Figure 1. The calibration curve, Figure 2, was derived from the absorbance values plotted against the percent PVA per 100-mL at λ max. During the oxidation of PVA the percent amount of PVA left in solution was determined by transferring 0.1 mL of the solution to 100-mL flask already containing 20 ml of 4% boric acid solution and 6 mL of iodine solution. The 100-mL flask was brought to volume with distilled water (dilution factor of 1000). After shaking the contents of the flask to ensure uniformity, the absorbance of the sample was taken at λ max and the result compared to the calibration curve. During the mixing and agitation of the flask content the sample was discarded if blue/green precipitates were observed.

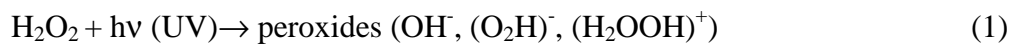
The calibration equation for the percent PVA versus absorbance profile in Figure 2 is linear. Where,

$$Y (\%PVA) = 0.0022 X (\text{absorbance}) - 0.000003$$

Photochemical oxidation of PVA in hydrogen peroxide

Hydrogen peroxide was added to the PVA solution and its decomposition rate to form hydroxyl radicals at room temperature enhanced with UV light. The generated peroxides (hydroxyl radicals) then reacted with the PVA, initiating a rapid cascade of oxidation reactions that ultimately mineralize the PVA as depicted below (Jaeger et al. 1979).

In equation 1 below the photo-dissociation of hydrogen peroxide results in the production of powerful oxidizing radicals (hydroxyl, hydroperoxide, peroxonium and peroxide ions).

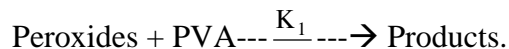


The peroxides are the principle agents responsible for the oxidative mineralization of PVA (equation 2). Per equation 1 and 2 the oxidation of PVA is a complex and irreversible consecutive set of reactions.

A Pyrex[®] glass sample receptacle was used for all the UV studies because it shows a greater than 90% UV transmission above 300 nm (Winer 1979). For the UV lamps, the corresponding energies per mole are, respectively, 327 kJ/mole (longer wave UV energy source at 366 nm), 396 kJ/mole (intermediate long wave at 302 nm), and 471 kJ/mole (short wave at 254 nm). The energy data are obtained by converting wavelength in nm to energy units E (kJ/mole), that is, $E = 1.1962 \times 10^5 / \lambda$ kJ/mole.

Since quantitative calculation for this complex photo-dissociation of H₂O₂ is not straightforward (Korman et al. 1988), the apparent reaction rate constant for the mineralization of PVA in the presence of H₂O₂ was based on initial PVA concentration and its concentration changes with time only as shown below.

From equation 2 above,



$$-d[\text{PVA}]/dt = K_1[\text{peroxides}] [\text{PVA}] \quad (3)$$

If equation 4 is integrated, noting that at time, $t = 0$, concentration of products = 0, then

$$\text{Ln} [\text{PVA}]_0 / [\text{PVA}]_t = K_1[\text{Peroxides}]\tau \quad (4)$$

If it is assumed that $K_1[\text{Peroxides}] = \text{constant}, K_2$, (where τ is time), then

$$\text{Ln} [\text{PVA}]_0 / [\text{PVA}]_t = K_2\tau \quad (5)$$

A plot of the left-hand side of equation 5 versus τ should yield a straight line with the slope equal to K_2 . Here, we have assumed that K_2 represents the apparent reaction rate constant for the oxidative mineralization of PVA.

The UV light intensities (at 1 cm) on the irradiated PVA/H₂O₂ samples in a circular petri dish are calculated as power per unit area of exposure or Watt per square meter. For the petri-dishes (5.7 cm by 1.2 cm) the intensity is $6 \text{ Watt}/(0.785)(5.7 \text{ cm}^2) = 2,352.5 \text{ Watt/m}^2$.

The oxidation of a mixture of 5% PVA solution with hydrogen peroxide at room temperature required about two weeks aging to obtain a better than 90% mineralization of 5% PVA solution. This was the case even when the PVA and hydrogen peroxide were in a 1:1 ratio by volume. The oxidation of PVA with hydrogen peroxide with sonochemical treatment and without UV light showed a small increase in reaction rate over PVA

oxidation with H_2O_2 only. The average time required for a complete oxidative mineralization of PVA was reduced by 24%. To enhance the oxidation rate of PVA in the presence of hydrogen peroxide, sonochemical (ultrasonic irradiation) and UV photochemical (ultraviolet light irradiation) techniques were employed.

In runs where ultrasonic energy was used to further enhance the oxidation of PVA, a 20 kHz ultrasonic generator energy output was maintained at 4.58 Watts/cm^2 . Here it is assumed that there is a minimum ultrasonic intensity below which there is no enhanced degradation of PVA in the presence of H_2O_2 . Based on the work of Mostafa (1958), 3.125 Watts/cm^2 was chosen as this threshold intensity for PVA. The test samples were either put in a 150-mL Teflon[®] beaker or in a 150-mL pyrex[®] glassware. For simultaneous sonication and UV irradiation treatment of the PVA in hydrogen peroxide samples, the UV lamp was aligned along the side of the beaker inside an ultrasonic chamber. In oxidation reactions not involving sonication the PVA/hydrogen peroxide mixtures were put into 5.7 cm by 1.2 cm petri dishes sitting on a small laboratory jack under the mercury UV lamp.

Two principal UV wavelengths (302 and 366 nm) were evaluated for the photochemical oxidation of PVA in the presence of H_2O_2 . There were no appreciable improvements on reaction rate over PVA oxidation with only H_2O_2 when photochemical treatment of PVA at 254 nm was carried out in the presence of H_2O_2 .

No measurable PVA oxidation changes were observed with just treating 5% PVA solutions with ultrasonic energy at 90 Watts for three minutes. Faster oxidation rates for

the mineralization of PVA with UV in the presence of H_2O_2 were obtained only with 302 and 366 nm UV treatments.

RESULTS AND DISCUSSION

PVA oxidation at 366 nm

Basically two types of PVA oxidation runs were performed: oxidation of PVA in H_2O_2 with ultraviolet irradiation only and PVA in H_2O_2 oxidation with both ultrasonic and ultraviolet treatments. The oxidation of PVA/ H_2O_2 mixtures (5 to 33% H_2O_2 by volume relative to total PVA solution volume) coupled with UV treatment at 366 nm, was performed in petri dishes. In the second type of oxidation runs (PVA/ H_2O_2 oxidation with ultraviolet and ultrasonic energy), each sample mixture was put into 150-mL Teflon[®] or Pyrex[®] glass beaker and sonicated (ultrasonic energy maintained at 4.6 Watts/cm²) for three minutes initially and then exposed to UV light at 366 nm. The samples could also be sonicated continuously at a given time interval while it was being treated with UV light. For these runs, at intervals of 20-30 minutes, 0.1 ml samples were collected and quantified for percent PVA left in solution. This was performed until a better than 90% conversion of PVA was attained. Figure 3 shows a typical decay curve for PVA oxidation in H_2O_2 coupled with sonication and UV light at 366 nm.

In theory the approximate UV exposure time, τ , can be obtained by solving equation 5. However, because of the assumption that $K_2 = K_1$ [peroxide], τ values obtained by solving equation 5 are in error since the concentration of the peroxides are unknown. As a result, τ values were determined experimentally.

Figure 4 shows an overlay plot of data obtained with PVA oxidation at 366 nm, with and without sonication, in the presence of H₂O₂. Slopes in Figure 4, which are the reaction rate constants, are respectively, 0.0219 min⁻¹ for oxidation with initial sonication for three minutes before exposure to UV at 366 nm and 0.0176 min⁻¹ without sonication. Based on the magnitude of the reaction rate constants the conclusion is made that PVA oxidation in the presence of hydrogen peroxide and UV light coupled with sonication is faster.

In continuous sonicated and UV treated runs, samples under UV lights were sonicated for three minutes at intervals of 30 minutes, with ultrasonic energy maintained at 90 Watts. Care must be exercised in the use of 100-mL Pyrex[®] beaker as sample container for the sonication. The beaker must contain sufficient sample solution, at least 50 ml, to prevent the shattering of the beaker due to ultrasonic energy. At intervals of 20 minutes aliquot samples (0.1 mL) were collected for analysis and determination of percent of PVA left in solution. This was performed until more than 90% of the PVA was mineralized. With this combined sonication and UV treatment of PVA /H₂O₂ mixtures the reaction time, τ , was further reduced from hours to minutes for both oxidation at 366 and 302 nm.

Table 2 shows a summary of PVA oxidation data with UV/H₂O₂ coupled with sonication treatment for various proportions of H₂O₂ in 5% PVA. This table also contains the calculated average reaction rate constants, the average UV illumination time (τ) needed to obtain a better than 90% oxidation of 5% PVA and corresponding proportions of H₂O₂ in 5% PVA. The first part of Table 2 (column 2 through 5 for oxidation with 17.6% H₂O₂) shows a set of data for oxidation without sonication treatment for comparison. Oxidation reaction rate for PVA at 17.6% H₂O₂ composition with sonication is about

twice as fast when compared with oxidation without sonication. In addition, τ time is reduced from 233 minutes to 60 minutes with sonication.

PVA oxidation at 302 nm

The same procedure, as described above, for oxidation of PVA at 366 nm was repeated with the UV lamp wavelength changed to 302 nm.

Figure 5 shows a typical overlay plot for PVA oxidation profile per equation 6 for PVA oxidation at 302 and 366 nm with sonication. The reaction rate constants per equation 6 for PVA oxidations at 302 and 366 nm are, respectively, 0.0966 and 0.061 min⁻¹. The magnitude of the reaction rate at 302 nm is about 37 % higher than the reaction rate at 366 nm, which indicates a faster reaction rate at 302 nm.

The first four columns in Table 3 contain a summary of 5 % PVA/H₂O₂/UV oxidation data at 302 nm with and without sonication. The last four columns in Table 3 show a summary of the average data obtained for 5% PVA oxidation with UV at 302 nm coupled with continuous sonication of the reacting mixtures of PVA and H₂O₂. Based on the magnitude of the reaction rate constant data the reaction rate for the sonicated PVA/H₂O₂ treatment at 302 nm is on the average about a factor of 3 better than runs without sonication. In all cases, the plot shows that the time for a better than 90% conversion of PVA into smaller molecules (τ) is higher for all PVA/ H₂O₂ reaction mixtures that were not sonicated during mineralization. Overlay plots in Figure 6 show illumination time (τ) versus percent H₂O₂ for PVA oxidation with and without ultrasonic treatment at 302 nm. Similarly, overlay plots in Figure 7 shows the reaction rate constant

versus percent H₂O₂ used in PVA oxidation at 302 ηm with (slope of 5.8) and without ultrasonic treatment (slope of 1.2). Again, as expected, reaction rates are higher for all sonicated PVA/H₂O₂ oxidation runs.

During some of the PVA/H₂O₂ oxidation runs with sonication, changes in the solution matrix pH with oxidation time were monitored (Figure 8 is a typical plot). By the time the oxidation of 5% PVA was almost complete the pH had dropped from a value of about 5 down to 2.5.

Three different oxidation reactions of 5% PVA at 302 ηm were carried out at temperatures of 28 °C, 45.6 °C and 58.6 °C. The duration of ultrasonic treatment was used as a means of increasing the reaction temperature of the mixtures. That is, the longer the sonication time the higher the reaction temperature of the PVA/H₂O₂ reaction mixture. In these particular PVA/ H₂O₂ oxidation runs a thermocouple was inserted into the reaction mixture and the system calibrated to ascertain the number and duration of ultrasonic pulses that will give the desired temperature in the reaction mixture.

Table 4 contains a summary of the reaction rates at different temperatures. The reaction rates increased with increasing reaction temperatures. Figure 9 is a plot of the natural log of the reaction rate constants versus the reciprocal of the reaction temperatures in degrees Kelvin. The slope of the line in Figure 9 is -3138.

The slope of the line = -E_a (activation energy)/R (gas constant).

$$E_a = 3138 (8.3144) \text{ JK}^{-1} \text{ Mole}^{-1} = 26,091 \text{ JK}^{-1} \text{ Mole}^{-1}$$

The calculated activation energy under these conditions is therefore approximately 26,000 JK⁻¹ Mole⁻¹.

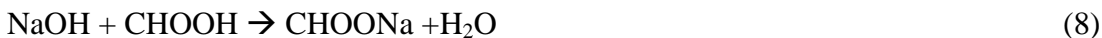
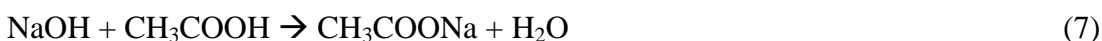
PVA photochemical and sonochemical oxidation products.

The oxidation products from the mineralization of PVA in hydrogen peroxide with only ultraviolet irradiation at both 302 and 366 nm gave a colorless, transparent solution, which we chromatographically identified as mainly acetic acid (Finch 1992). However, the oxidation products from combined ultraviolet irradiation and ultrasonic treatment of PVA in hydrogen peroxide gave a colored solution with a yellow tinge. Based on chromatographic data, we obtained a mixture of acetic and formic acids. This observation is also in agreement with findings of other researchers (Ikada et al. 1977 and Mino et al. 1959). The observed color difference seems to indicate that there exists an intrinsic difference in reactivity between radicals formed by photolysis and those formed by ultrasonic treatment (Takahide et al. 1998), which would result in the formation of different end products during the oxidation of PVA. It is worth noting that the oxidation of PVA with potassium permanganate has been reported to produce mainly oxalic acid and carbon dioxide (Finch 1992).

In addition to its stringent high alkaline requirement (pH > 10) for corrosion and organo-nitrate controls, the requirements for a nuclear wastewater treatment facility includes the control and minimization of wastewater solid content, salts in particular, is of prime importance for meeting wastewater processing requirements. The main products from

hydrogen peroxide-based oxidative mineralization of PVA have been identified mainly as acetic and formic acid.

The pH of the resulting solutions ranged from 2.7 to 3.1. Since the pH of a completely mineralized PVA solution is acidic and will need to be adjusted to a value greater than 10 in order to meet waste acceptance criteria for processing with other waste streams in a nuclear waste facility, the amount of salts generated must be determined. To estimate the amount of organic salts formed from pH adjustment to 13.5 with sodium hydroxide, 50 ml of our oxidized PVA solution was titrated with 1.0 molar solution of sodium hydroxide. 15 mL of 1.0 molar solution of sodium hydroxide was required to bring the pH of the oxidized PVA solution to a pH value of 13.5. This is equivalent to 12 g of sodium hydroxide per liter of completely oxidized 5% PVA solution. If one assumes that the pH adjustment results in the conversion of all the acids in solution to their corresponding acetate and formate salts of sodium per equation below, then the amount of salt formed can be estimated:



From equation 8 above, stoichiometrically, 82 g of sodium acetate salt is produced from the neutralization reaction per 40 grams of sodium hydroxide used. Therefore 24.6 grams of the acetate salt will be produced per liter of oxidized PVA solution (82 g acetate/40 g NaOH * 12 g NaOH). Similarly per equation 9 above, 68 g of sodium formate is produced

from the neutralization reaction with 40 g of sodium hydroxide. This means 20.4 g of sodium formate is produced per liter of oxidized PVA (68 g formate/40 g NaOH* 12 g NaOH).

If one assumes that a liter of completely oxidized PVA solution contains only acetic and formic acids in a 1:1 ratio then the estimated average amount of salt in that solution would be 45 grams of salt per liter of oxidized PVA solution. Since the estimated percent-oxidized PVA solution volume is about 2% in a typical nuclear wastewater processing facility, this translates to about 3,400 kilograms of water-soluble salt in a 3.8 million-Liter (million gallons) nuclear wastewater storage tank

Evaporation and compatibility of oxidized PVA solution

Two, three and four percent PVA solutions were prepared by serial dilution of neat five percent PVA solutions. Portions of each PVA solution (500-mL) were put into 1000-mL beakers on a temperature-programmed hot plate for continuous evaporation. The temperature of the hot plate was gradually raised by 10 °C every 20 minutes. The temperature of each heated beaker and its contents was monitored regularly. The behavior of each PVA solution (2, 3, 4 and 5% PVA) was monitored by looking for the formation of films of transparent PVA material on the beaker walls and around the general evaporation surface. The above evaporation experiments were repeated with completely mineralized PVA solutions from oxidations with and without ultrasonic treatment. The evaporation beakers containing neat PVA solutions started showing evidence of formation of PVA films (skins) at about 70 °C. By the time the temperature of each solution had reached 85 °C the entire evaporation surface of each beaker had been covered with thin transparent sheet of PVA film. After about six hours on the hot plate

(average temperature of 98 °C) each of the beakers had lost all its water content and only the PVA film residue was in each beaker. With oxidized PVA solutions, under the same evaporation conditions, there were no films formed and after about six hours there were no residue materials left on the bottom of each beaker.

To evaluate for interactions between nuclear process wastewater simulant and oxidized PVA solutions equal volumes of oxidized PVA and nuclear process wastewater simulant were mixed in 50-mL sampling vials. Similar experiment was repeated with neat PVA solutions. In the test, the pH of the oxidized PVA solution was adjusted with 1.0 molar solution of sodium hydroxide until the solution pH was about 13.5. The resulting solution was treated with ultrasonic energy until all the excess hydrogen peroxide had been decomposed. This oxidized PVA solution, without excess H₂O₂, was also mixed with nuclear process wastewater simulant on a one-to-one basis.

The mixing of even trace amounts of neat and unmineralized PVA solution with nuclear process wastewater simulant resulted in the formation of white “fluffy cotton ball” precipitate or suspensions in solution. This led to the existence of two distinct phases. With about one percent of the neat PVA in the simulant solution a clearly white fluffy ball suspension was formed at room temperature.

The mixing of a better than 90% oxidized PVA solution with nuclear wastewater simulant, even on a one-to one basis, produced no visible solid particles or precipitates. However, at the instant of blending the two solutions together the resulting mixture

turned orange, probably due to the oxidation of sulfur, which is present in trace amounts in the nuclear process wastewater simulant. Since excess hydrogen peroxide was present in oxidized PVA solution the mixing of oxidized PVA with nuclear wastewater simulant led to the evolution of gases. This was probably due to the decomposition of hydrogen peroxide in an alkaline environment. The mixing of oxidized PVA solution, in which excess hydrogen peroxide had been removed, with nuclear process wastewater simulant did not result in the evolution of gases and no precipitation of solid particles were also observed. Therefore, before mixing of oxidized PVA waste with other nuclear process wastewater excess H_2O_2 must be removed by adjusting the pH to an alkaline condition.

Nuclear process wastewater simulant spiked with two or more percent completely oxidized PVA solution, when evaporated to dryness contained no PVA evaporation residue, scales or films of PVA. With a drop in temperature (test samples left overnight) there was still no film or scaly evaporation products formed. Salt crystals from the simulant itself were formed during the heating and evaporation of the oxidized PVA and nuclear process wastewater simulant.

The average nuclear process wastewater simulant composition used in this study is summarized in Table 5. The simulant, with an average sodium ion concentration of 5.6 molar, was spiked with 2% oxidized PVA solution. This 2% value is considered a conservative representation of the volume of oxidized PVA per a given nuclear process wastewater storage tank. This spiked solution was used in the characterization of cesium-137 and plutonium-239 removal efficiencies with CST and MST ion exchange materials. A diluted spiked solution of the nuclear wastewater simulate (4.7 M Na^+), was used for

the characterization of cesium-137 removal from the nuclear wastewater using TPB. The sorption of radionuclides present in a nuclear process wastewater simulant as spiked ions (cesium onto CST, cesium onto TPB, and Plutonium and strontium-90 onto MST) was studied by batch technique. The general method used for these studies is described below. The batch distribution coefficient (K_d) is an equilibrium measure of the overall ability of a solid phase ion exchange material to remove ions of interest from solution. It represents the theoretical volume of solution that can be processed per a given mass of the ion exchanger under equilibrium conditions (Klavetter et al.). In these tests, a known quantity of each sorbent (≈ 0.1 g) was placed in contact with 25 ml of the simulant in a 50-ml polyethylene bottle. All samples were prepared in duplicates. The polyethylene bottles were placed in an orbital shaker and the mixture agitated for a given period at room temperature. After this contact time, the used sorbent material was separated from the solution by filtering through a 0.2 micron-nylon filter. The liquid fraction, without sorbent, was submitted for metal concentration analysis. The K_d value was obtained by determining the concentration (or activity for radionuclides) of metal ions of interest before and after contact and calculating the amount of metal ions of interest on the sorbent by difference.

For radioactive samples or simulants spiked with radionuclides, K_d values were determined radiometrically by using the following equation:

$$K_d = ((A_i - A_f)/A_f)(V/m) \quad (9)$$

Where A_i and A_f are the activities of the radionuclide in solution at the beginning and at the end of sorption respectively, V is the volume in ml of the solution used for equilibration and m is the weight of the adsorbent in grams.

The decontamination factor, D_f , is defined as initial concentration over final concentration.

The determination of changes in the batch distribution coefficient, K_d , and decontamination factor for the uptake of radionuclides in the presence of nuclear process wastewater simulant (5.6 M Na^+) spiked with 2% oxidized PVA was carried out in the following manner. A 25-mL of the selected liquid per mixing vial was spiked with 0.5 ml Cs-137 (tracer) and mixed for 5 minutes. After mixing for 1 minute, 1.0 ml of the sample was sent for counting to get initial Cs-137 concentration. 1.0 g of CST was then added into each vial and the slurry mixed for 30 minutes and filtered through a 0.25-micron syringe filter. One milliliter of the filtrate was sent for gamma counting to obtain cesium-137 left in solution. Based on equation 9 above, the batch distribution coefficient, K_d , was determined. The K_d for nuclear process wastewater simulant (5.6 M Na^+) containing no oxidized PVA was also determined in a similar fashion.

In evaluating changes in the decontamination factor, D_f , using TPB, 25 ml of the nuclear process wastewater simulant (4.7 M Na^+) and nuclear process wastewater simulant (4.7 M Na^+) containing 2% by volume oxidized PVA solution, were spiked with 0.75 mg cold cesium and 1.0 ml of cesium-137 tracer. Initial cesium activity was in the range of 1.98 to 2.21E05 d/min/mL. 0.4 gm of sodium tetraphenyl borate (NaTPB) was added to each solution and stirred. At the end of 30 minutes, the cesium-137 activity from the filtrate

for each sample was determined. Similarly, 25 ml of the solutions (nuclear process wastewater simulant (5.6 M Na⁺) and nuclear process wastewater simulant containing 2% by volume oxidized PVA solution) were spiked with Sr-90. The samples were treated with flow-sheet-level monosodium titanate slurry and the solutions agitated overnight. Samples for analysis were syringe filtered before submission for analysis. The above procedure was repeated with plutonium-239 tracer. Based on equation 9, the decontamination factors for cesium-137, strontium-90 and plutonium-239 were calculated.

The results for the sorption of some representative nuclear process wastewater radionuclides (Cs-137, Sr-90, and Pu-239) are summarized in Table 6. The CST ion exchange material K_d values for Cs-137 extraction from simulated waste solution (2366 ml/g) is comparable with the K_d value for Cs-137 extraction with CST in the same simulant containing 2% oxidized PVA (2354 ml/g). The magnitudes of the D_f values for Cs-137 extraction with TPB in the simulant and PVA spiked simulate are, respectively, 282 and 302. Based on the level of uncertainties in K_d measurements for these sorbents, these two numbers are not statistically different. The same is true for the magnitude of both K_d and D_f -values for Pu and Sr extraction from PVA spiked and unspiked simulant with MST (Table 6). Therefore, there are no significant differences between mineralized PVA spiked simulant and the neat simulant in their respective magnitudes of K_d and D_f value for the uptake of radionuclides.

Although a measure of D_f and K_d values above indicate no effects on ion-exchange properties in the presence of oxidation products, the potential exists for the complexing of

products of PVA oxidation and even hydrogen peroxide with radionuclides like plutonium and other actinides. The extent of complexing of each radionuclide with the oxidation products (acetates and formates from oxidation of PVA with H_2O_2) depends on the pH of the final waste stream. At high pH conditions, depending on the oxidation states of plutonium species present in any waste stream, the potential for the formation of plutonium hydroxides increases. These hydroxides of plutonium may eventually precipitate.

Equal volumes of completely oxidized PVA and neat unadulterated PVA were analyzed for total organic carbon content. The average total organic carbon for neat 5% PVA and completely oxidized PVA solutions were, respectively $25,700 \pm 200$ mg/L and $18,900 \pm 310$ mg/L. This is about 27 % less carbon in oxidized PVA. This difference in total organic carbon may be attributed to reactions leading directly to the formation of oxides of carbon such as carbon dioxide gas.

CONCLUSIONS

The oxidation of PVA solution with hydrogen peroxide with and without ultrasonic treatment produces no solids particles.

PVA oxidation products are mainly acetic, formic and oxalic acids. These carboxylic acids, in the presence of a neutralizing base like sodium hydroxide, are converted to their corresponding salts. The pH of completely mineralized PVA solution based on hydrogen peroxide oxidation is less than 3. Hence, pH adjustment with preferably sodium hydroxide would be required to bring the pH value above 10. Excess hydrogen peroxide

will also have to be destroyed by heating the oxidized PVA waste solution between 70-80 °C. This destruction of excess hydrogen peroxide can be successfully accomplished during pH adjustment by applying ultrasonic energy to the oxidized PVA waste.

The oxidation of 5% PVA in the presence of UV light at 302 nm coupled with continuous ultrasonic treatment provided the best PVA oxidation results. Based on neutralization reactions between acidic solutions from PVA oxidation products and sodium hydroxide, the amount of organo-sodium salts, which could be produced from pH adjustments of oxidized PVA solution (sodium acetate and sodium formate), were estimated. The estimated amount of combined soluble sodium salts produced from pH adjustment reactions is about 45 g per liter of mineralized 5% PVA processed.

The magnitude of the batch distribution coefficient and decontamination factors for radionuclide removal with ion exchange materials was found to be equal for nuclear process wastewater simulant solutions with and without 2% oxidized PVA. Therefore, efficiencies for cesium-137, strontium-90, and plutonium removal from the nuclear wastewater, using ion exchange sorbents (CST and MST) and precipitating agents (TPB) are not affected by the presence of oxidized PVA. The chelating or induced precipitation of the radionuclides in the presence of the carboxylic moieties from the oxidation of PVA, under alkaline conditions, is also unlikely.

Plutonium in its lower oxidation states (Pu^{+3} and Pu^{+4}) and in low pH conditions for example, readily forms weak acetate ($\text{Pu}(\text{C}_2\text{H}_3\text{O}_2)^{2+}$) and oxalate ($\text{Pu}(\text{C}_2\text{O}_4)_2^+$)

complexes and possibly formate complexes ($\text{Pu}(\text{HCO}_2)^{2+}$), too (Cleveland 1979). Plutonium in higher oxidation states complexes less effectively with these organic species. These organic moieties (acetate, formate and others), which are by products of PVA oxidation will form stable complexes with plutonium under low pH conditions as mentioned above. Therefore, to eliminate the potential for the formation of these Pu-organic complexes, it is necessary to perform pH adjustment ($\text{pH} > 10$) with mineralized PVA wastes, which are eventually mixed with other nuclear process wastewater.

On the other hand, weak organic complexes, such as those formed between organic moieties and plutonium ion may be destroyed under radiolytic conditions such as those present in a nuclear process wastewater treatment facility.

It is also worth noting that at high pH conditions, depending on the oxidation states of plutonium species present in any waste stream, the potential for the formation of plutonium hydroxides increases. These hydroxides of plutonium would eventually precipitate. Plutonium is capable of complexing with hydrogen peroxide in acidic conditions ($\text{pH} < 3$) to form a plutonium peroxy-complex $[\text{HO-Pu-OO-Pu-OOH}]^{4+}$. Hydrogen peroxide is destroyed by strong base. Therefore, addition of sodium hydroxide during pH adjustment, just before discharging mineralized PVA laden waste to nuclear process wastewater tanks, would destroy excess H_2O_2 and any Pu- H_2O_2 complexes.

There are several other approaches to the oxidative degradation of PVA in the presence of hydrogen peroxide. Surface modification of transition metal oxide catalysts such as

TiO₂ or doping of lanthanides (Augugliaro et al. 1990, Maurer, and Tanaka et al. 1989) and the application of photo-Fenton reactions (Bauer et al. 1997, Kiwi et al. 1994, Wei et al 1990 and Walling 1975), to name a few, are also available. However, these other organic degradation enhancement techniques may not be compatible with the nuclear process wastewater treatment facilities. For example, these techniques require the introduction of solid catalyst materials into the waste stream. Above all, these catalyst-based enhancement techniques seem to perform well only with solutions containing low ppm levels of organic compounds. In addition, solid catalysts in ppb levels may introduce unwanted side reactions under high alkaline conditions in the nuclear waste storage tanks. Since the pH of the final PVA waste solution will be adjusted to alkaline conditions the potential for the formation of explosive organo-nitrates in the nuclear process wastewater storage tanks would be eliminated.

Waste solutions containing better than 90% mineralized PVA, when mixed with nuclear process wastewater, are not expected to adversely affect the rheological (pumpability, PVA film formation, coagulation and precipitation of solid PVA) and evaporation (film formation) properties of the nuclear process wastewater. The viscosity of a completely mineralized 5% PVA solution is about 1.0 centiPoise as opposed to 32 centiPoise for neat unadulterated 5% PVA solution (Maurer). The density of oxidized PVA is 0.99 g/cc and that of neat 5% PVA solution is 1.05 g/cc. The pH of freshly prepared 5% PVA solutions is approximately 7 and with time it drops to less than 7.

No radiolysis or hydrogen generation experiments were performed with oxidized PVA solutions in the nuclear process wastewater simulants to evaluate the long or short-term effects of radiation on the stability of oxidized PVA products (Acetate and formate anions from PVA oxidation with H_2O_2). However, based on aqueous radiolytic chemistry, the introduction of oxidized PVA solution into a nuclear process wastewater system will not increase the production of flammable gases during storage and processing. Radiolysis of acetate and formate anions will produce mainly oxides of carbon as stable radiolytic products. Since the oxidation of PVA will be carried out in an open oxygen-rich environment, methane formation is highly unlikely. Thus, we conclude that the addition of oxidized PVA solutions into a nuclear process wastewater system does not increase the production of flammable compounds during storage and processing.

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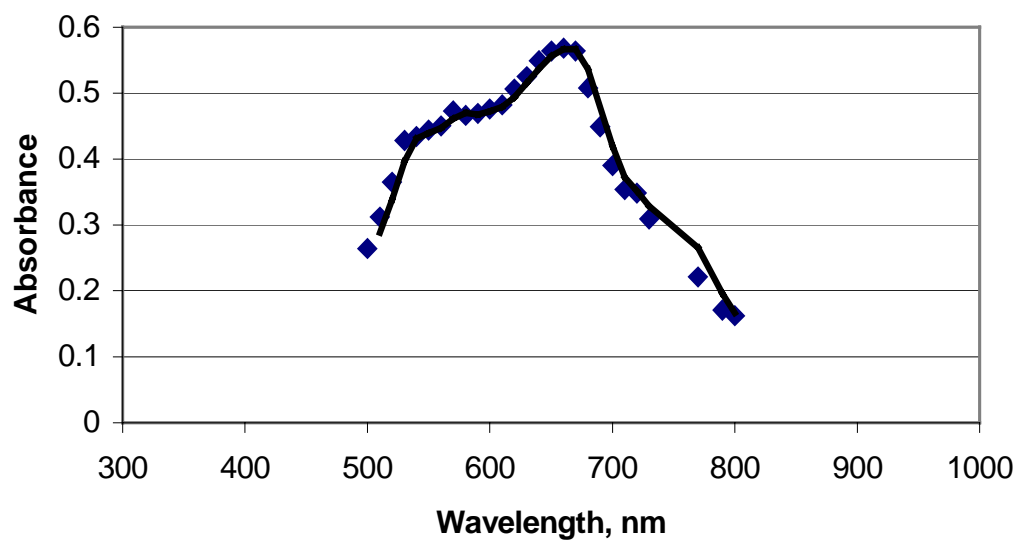


Figure 1. Absorption profile for PVA/Iodine/boric acid complex. λ -max. at 670 nm.

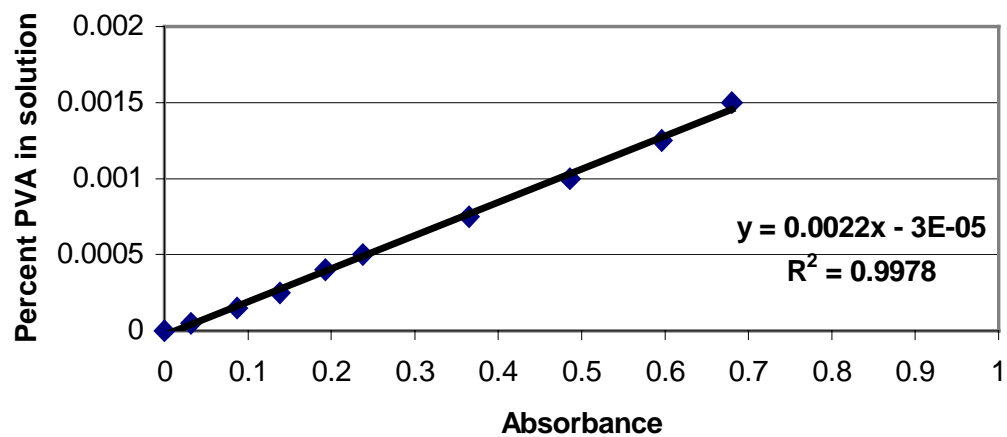


Figure 2. PVA calibration curve based on Iodine/boric acid/PVA complex absorbance at 670 nm.

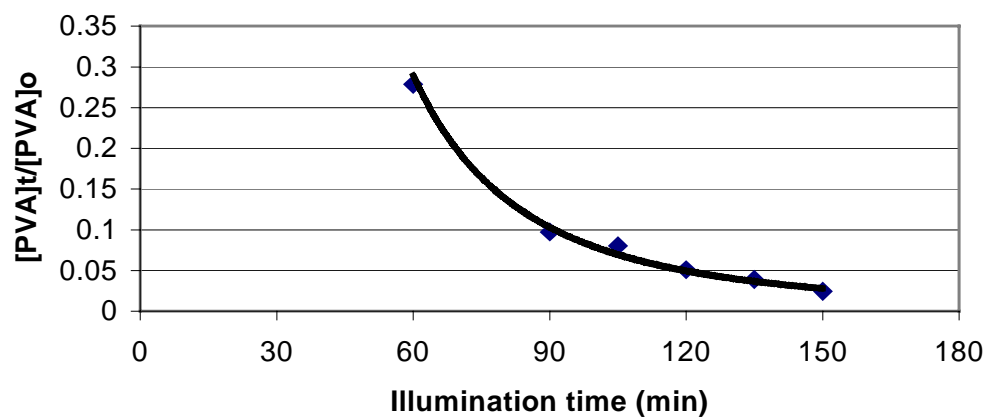


Figure 3. A typical decay curve for PVA oxidation with H_2O_2/UV at 366 nm with ultrasonic treatment.

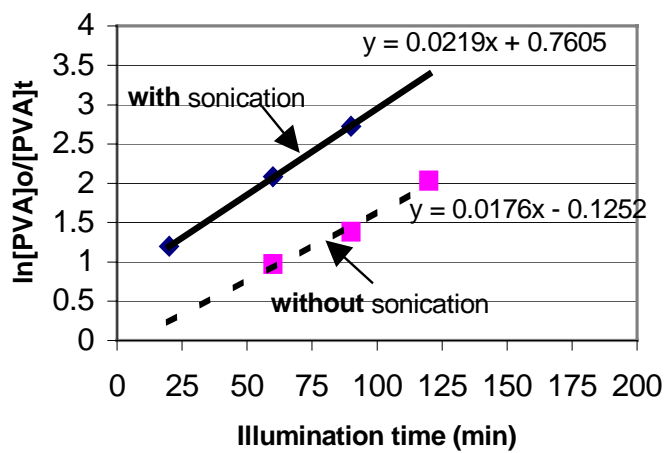


Figure 4. Plots per equation 5 for oxidation with and without ultrasonic treatment with UV light at 366 nm. Sonicated samples show higher reaction rates.

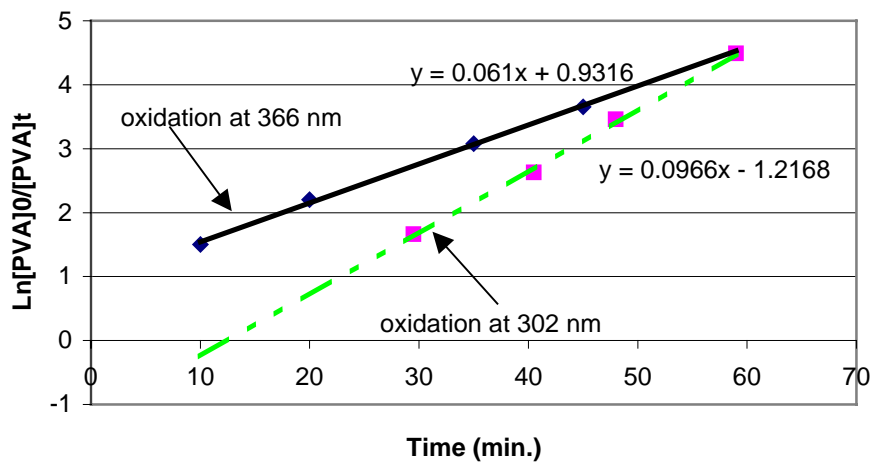


Figure 5. A typical PVA oxidation profile per equation 5 for oxidation at 302 and 366 nm.

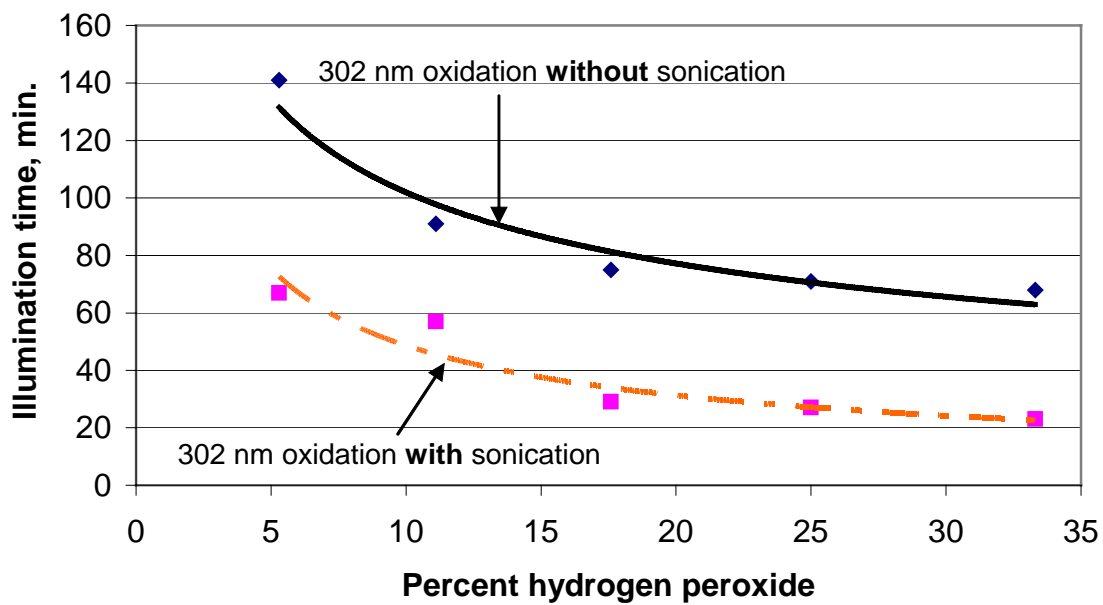


Figure 6. Variation of illumination time (τ) with percent hydrogen peroxide at 302 η m.

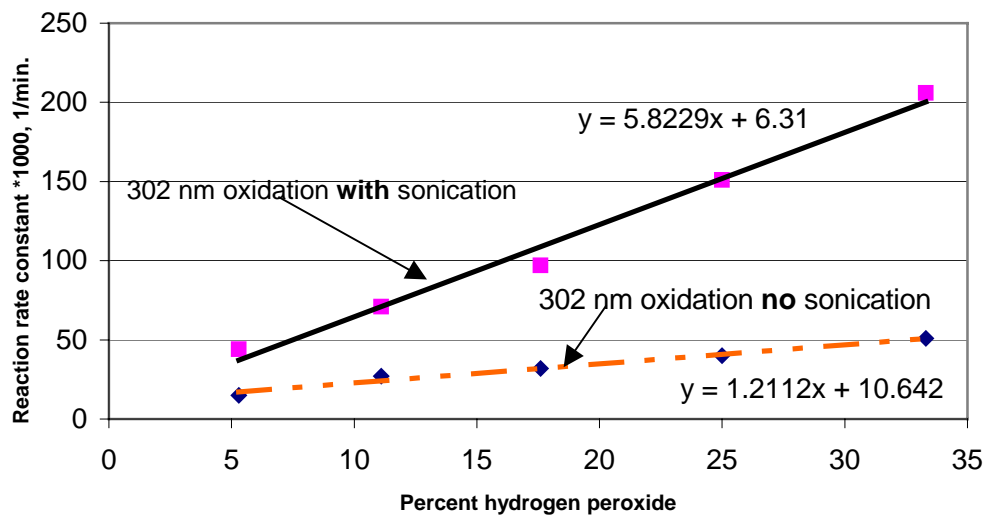


Figure 7. Changes in reaction rate constant with percent hydrogen peroxide used in mineralization of 5% PVA solution at 302 nm. Reaction rates are higher with sonication.

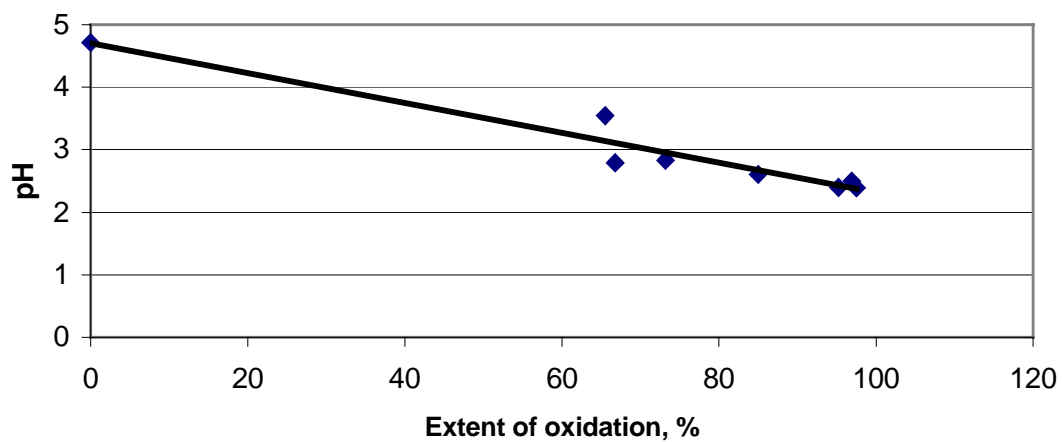


Figure 8. pH changes with extent of oxidation for PVA oxidation at 302 nm with ultrasonic treatment.

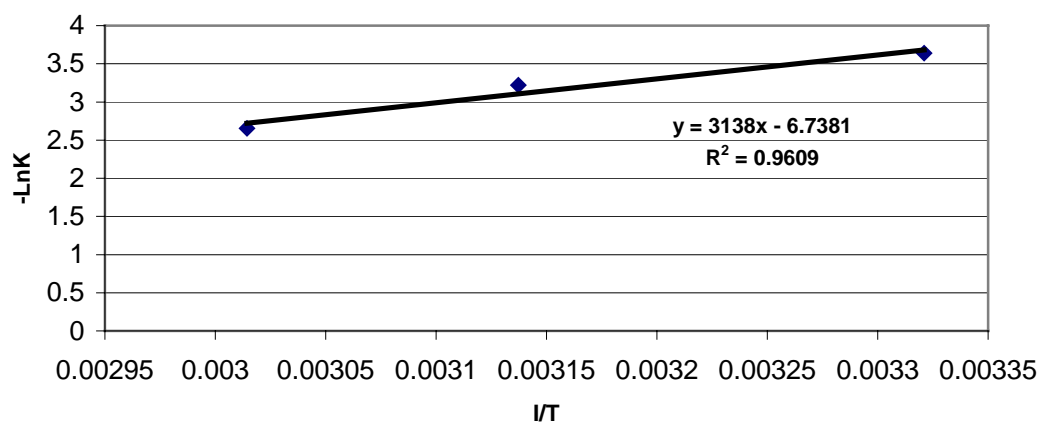


Figure 9. Activation energy plot for PVA oxidation with H_2O_2/UV at 302 nm with ultrasonic treatment.

Figure 1. Absorption profile for PVA/Iodine/boric acid complex. λ -max is 670 nm.

Figure 2. PVA calibration curve based on Iodine/boric acid/PVA complex absorbance at 670 nm.

Figure 3. A typical decay curve for PVA oxidation with H_2O_2 /UV at 302 nm with ultrasonic treatment.

Figure 4. Plots per equation 5 for oxidation with and without ultrasonic treatment with UV light at 366 nm. Sonicated samples have higher reaction rates constant values.

Figure 5. A typical PVA oxidation profile per equation 5 for oxidation at 302 and 366 nm.

Figure 6. Variation of illumination time (τ) with percent hydrogen peroxide at 302 nm.

Figure 7. Changes in reaction rate constant with percent hydrogen peroxide used in mineralization of 5% PVA solution at 302 nm. Reaction rates are higher with sonication.

Figure 8. pH changes with extent of oxidation for PVA oxidation at 302 nm with ultrasonic treatment.

Figure 9. Activation energy plot for PVA oxidation with H₂O₂/UV at 302 nm with ultrasonic treatment.

Table 1. Typical set of calibration standards with absorbance values at λ max.

Standard #	mL of intermediate stock per 100 mL	% PVA in standard	Average absorbance
0	0.0 (iodine and boric acid in water)	0	0.0
1	1.0	0.00005	0.032 ± 0.006
2	3	0.00015	0.087 ± 0.010
3	5	0.00025	0.138 ± 0.006
4	8	0.00040	0.193 ± 0.010
5	10	0.00050	0.238 ± 0.014
6	15	0.00075	0.365 ± 0.008
7	20	0.00100	0.486 ± 0.012
8	25	0.00125	0.596 ± 0.010
9	30	0.00150	0.680 ± 0.007

Table 2. Summary of PVA oxidation data with H₂O₂ and UV at 366 nm.

%H ₂ O ₂	Without Sonication		With sonication		
	Rate*1000, min. ⁻¹	τ, min.	Rate*1000, min. ⁻¹	τ, min.	
33.3	11 ± 1.7	233 ± 4.4	58 ± 0.6	15 ± 0.3	0 . 9
20			33 ± 1.1	30 ± 0.7	
17.6			21 ± 0.5	60 ± 1.2	
12.5			18 ± 2.2	120 ± 0.9	
5.3			3 ± 0.2	300 ± 1.6	

Table3. Summary for PVA oxidation data with H₂O₂ and UV at 302 ηm.

%H ₂ O ₂	Without Sonication		With sonication	
	Rate*1000, min. ⁻¹	τ, min.	Rate*1000, min. ⁻¹	τ, min.
33.3	51 ± 1	68 ± 0.9	206 ± 4	23 ± 0.2
25	40 ± 0.6	71 ± 1.4	151 ± 1.3	27 ± 0.5
17.6	32 ± 0.6	75 ± 1.1	97 ± 2	29 ± 0.3
11.1	27 ± 0.3	91 ± 1.8	71 ± 1.4	57 ± 1.2
5.3	15 ± 0.4	141 ± 2.8	44 ± 0.9	67 ± 0.9

Table 4. Summary of activation energy data for PVA oxidation at 302 η m with ultrasonic treatment.

I/T (Kelvin)	Degrees centigrade	Rate constant, K (1/min.)	-Ln K
0.003321	28.0	0.0263	3.63818
0.003137	45.6	0.0400	3.21887
0.003014	58.6	0.0704	2.65356

Table 5. Average inorganic composition for a typical nuclear process wastewater simulant.

Target ion /precursor	Average molar concentration
Na ⁺ (from all sodium precursors)	5.6
Cs ⁺ / CsNO ₃	0.00014
K ⁺ / KOH	0.015
OH ⁻ / NaOH, KOH	1.191
NO ₃ ⁻ / NaNO ₃	2.140
NO ₂ ⁻ /NaNO ₂	0.52
AlO ₂ ⁻ /NaAlO ₂	0.31
CO ₃ ⁻² /Na ₂ CO ₃	0.16
SO ₄ ⁻² /Na ₂ SO ₄	0.15
Cl ⁻ /NaCl	0.025
F ⁻ /NaF	0.032
PO ₄ ⁻³ /Na ₂ PO ₄ .12H ₂ O	0.01
C ₂ O ₄ ⁻² /Na ₂ C ₂ O ₄	0.008
SiO ₃ ⁻² /Na ₂ SiO ₃ .9H ₂ O	0.004
MoO ₄ ⁻² /Na ₂ MoO ₄	0.0002

Table 6. Batch distribution coefficients (mL/g) and decontamination factors for removal of target radionuclides from nuclear process wastewater simulant.

Radionuclide /sorbent	K_d or D_f in 4.7 M Na⁺ simulant	K_d or D_f in 2% PVA spiked simulate (4.7 M Na⁺)	K_d or D_f in 5.6 M Na⁺ Simulant
Cs-137/CST	2366, K _d	2354 K _d	1619, K _d
Cs-137/TPB	282 (D _f)	302 (D _f)	249 (D _f)
Sr-90/MST	20 (D _f)	19 (D _f)	Not applicable
Pu-MST	>30 (D _f)	23 (D _f)	21 (D _f)

Table 1. Typical set of calibration standards with absorbance values at λ max.

Table 2. Summary of PVA oxidation data with H_2O_2 and UV at 366 nm.

Table 3. Summary for PVA oxidation data with H_2O_2 and UV at 302 nm

Table 4. Summary of activation energy data for PVA oxidation at 302 nm with ultrasonic treatment.

Table 5. Average inorganic composition for a typical nuclear process wastewater simulant.

Table 6. Batch distribution coefficients and decontamination factors for removal of target radionuclides from nuclear process wastewater simulant.